series of subsidiary maxima on either side. As the thickness is increased, these subsidiary maxima come closer and closer, until in the limiting case one would not observe them at all (it would require an infinite resolving power for this), but only a uniform intensity corresponding to an average over a cycle. Performing this average, one obtains for the intensity an expression $1-|\tanh\alpha|$, where $\cosh\alpha=y$ of equation (2) (Ramachandran, 1944), which is identical with that given in Table 1 under Ewald. Incidentally, it may be noted that the dynamical theory also gives Prins's formula for an absorbing crystal (Kohler, 1933) from which Darwin's formula can be derived by the process given above. It is thus gratifying that the two theories, with their entirely different mathematical techniques, lead to identical results when the appropriate physical assumptions are put in.

It would be clear from the above that the problem of the Bragg reflexion by a perfect non-absorbing, or not sufficiently absorbing, crystal plate requires a more detailed specification of the conditions at the back of the plate. Ewald & Schmid (1936) have shown that, given any such specification, the exact intensity curve can be obtained from Ewald's solution by simple considerations of optical path without rediscussing the dynamics of field propagation. This can also be done by the Darwin method, using the mathematical procedure given by Ramachandran (1942, 1944).

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On the Patterson Transforms of Fibre Diagrams

By Carolina H. MacGillavry and E. M. Bruins

Laboratory of General and Inorganic Chemistry, and Mathematical Institute of the University, Amsterdam, Holland

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A method is given for the calculation of a two-dimensional Patterson transform from the intensity data of a fibre diagram. This vector map is a section parallel to the fibre axis through the cylindrically symmetrical three-dimensional Patterson transform of the fibre.

1. It has become a fairly general practice to begin the theoretical part of the X-ray analysis of single crystals by computing the Patterson diagram or vector map. This is the Fourier transform of the intensity data, and it offers a convenient synopsis of what can be derived about the crystal structure without introducing any assumptions.

From powder or 'amorphous' diagrams statistics of absolute values of atomic distances can be obtained from a similar transform, as Zernike & Prins (1927) have pointed out. (Since orientation is random in crystal powder or amorphous material, it is evident that no information whatever can be derived from these diagrams about the direction of the interatomic distances.) Warren and his school have used this method with considerable success in their investigations of glass, rubber, etc. The equivalent method of tackling the typical *fibre* diagrams, however, seems never to have been developed, and it was, therefore, considered worth while to fill this gap in the theory because the fibre texture is, in most macromolecular substances, the highest degree of orientation attained up to now.

2. In the following we confine ourselves to the ideal fibre texture, defined by (*a*) strict periodicity in the direction of the fibre axis, and (*b*) completely random orientation of azimuth round this direction. No assumptions need be made as to a more or less regular arrangement in directions other than the fibre axis.

As is well known, the intensity H scattered in a direction $\mathbf{s}$ by a density distribution $\rho(\mathbf{r})$ is, apart from trivial factors such as polarization, given by

$$H(\mathbf{h})=\int_{\mathbf{r}}\int_{\mathbf{r}'}\rho(\mathbf{r})\,\rho^*(\mathbf{r}')\exp\{2\pi i(\mathbf{h},\,\mathbf{r}-\mathbf{r}')\}\,d\tau_{\mathbf{r}}\,d\tau_{\mathbf{r}'},\quad(1)$$

where $\mathbf{h}=(\mathbf{s}-\mathbf{s}_0)/\lambda$, $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors of the primary and diffracted beams respectively, λ is the wave-length of the X-rays, and $d\tau_{\mathbf{r}}$ and $d\tau_{\mathbf{r}'}$ are volume elements.

Taking together contributions to the integral with fixed distance $\mathbf{r}-\mathbf{r}'=\mathbf{y}$, and introducing the Patterson function

$$\phi(\mathbf{y})=\frac{1}{V}\int_{\mathbf{r}}\rho(\mathbf{r})\,\rho^*(\mathbf{r}-\mathbf{y})\,d\tau_{\mathbf{r}},\quad(2)$$

where V is the irradiated volume, (1) becomes, as usual,

$$H(\mathbf{h})=V\int_{\mathbf{y}}\phi(\mathbf{y})\exp\{2\pi i(\mathbf{h},\,\mathbf{y})\}\,d\tau_{\mathbf{y}},\quad(1a)$$

the integral being extended over all the distances in the fibre.

It is convenient to introduce at this point cylindrical polar co-ordinates. The vector $\mathbf{y}$ will be given by its co-ordinate z in the fibre direction, the distance x from the fibre axis through the origin, and an azimuthal angle α. The scattering vector $\mathbf{h}$ (see Fig. 1) is defined by the corresponding Bernal co-ordinates ζ and ξ. The plane defined by $\mathbf{z}$ and $\mathbf{h}$ can be taken as the zero plane with respect to the azimuthal angle α. Then (1a) becomes

$$\frac{H(\zeta,\,\xi)}{V}=\int_{\alpha}\int_{z}\int_{x}\phi(z,x,\alpha)\times\exp\{2\pi i(\zeta z+\xi x\cos\alpha)\}\,x\,dx\,dz\,d\alpha.$$

Now, in a perfect fibre structure as defined above, though the density ρ of the single fibre may have no symmetry whatever, the distance distribution function $\phi(\mathbf{y})$ has axial rotation symmetry; any interatomic distance will be found with random azimuth around the fibre direction. This means that ϕ is a function of the co-ordinates z and x only. The integration over α can then be carried out immediately, giving

$$\frac{H(\zeta,\,\xi)}{V}=2\pi\int_{z}\int_{x}\phi(z,x)\,I_0(2\pi\xi x)\exp(2\pi i\,\zeta z)\,x\,dx\,dz,\quad(1b)$$

where $I_0(2\pi\xi x)$ is the Bessel function of zero order.

Since $\phi(z,x)=\phi(-z,x)$—combination of centro-symmetry with axial symmetry—the complex form $\exp(2\pi i\zeta z)$ can be replaced by $\cos(2\pi\zeta z)$. Moreover, ϕ is periodic in z, since this is true for ρ according to assumption (a). Thus

$$\phi(z,x)=\sum_{k}\phi_k(x)\cos 2\pi kz,\quad(3)$$

if the fibre period is for convenience normalized to 1. In the usual way, H is then found to be appreciable only for integral values of ζ, the integration giving for these values

$$\frac{H(k,\,\xi)}{V}=2\pi N\int_0^\infty\phi_k(x)\,I_0(2\pi\xi x)\,x\,dx,\quad(1c)$$

where N is the number of periods in the fibre direction.

By means of the integral equation (1c) each Fourier coefficient $\phi_k(x)$ in the sum (3) is connected with the intensity distribution $H(k,\,\xi)$ on the kth layer line of the fibre diagram. The $\phi_k(x)$ can be solved from these equations, for any value of x, by means of a well-known theorem on Bessel functions (Courant & Hilbert, 1931, p. 424). Thus

$$\phi_k(x)=\frac{2\pi}{NV}\int_0^\infty H(k,\,\xi)\,I_0(2\pi\xi x)\,\xi\,d\xi.\quad(4)$$

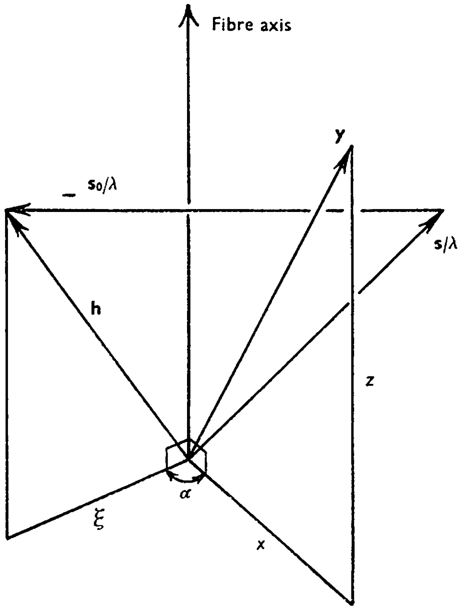

Fig. 1. Cylindrical co-ordinates of a vector in the fibre space and a vector in reciprocal space.

Equations (3) and (4) together define a two-dimensional Patterson function, containing all the information about interatomic distances which can be derived directly from the fibre diagram. In particular, $\phi_0(x)$ alone, the Bessel transform of the intensity on the equator, gives the radial distribution function of the projection in the direction of the fibre axis; it will provide information on the lateral packing of the chains.

3. Finally, although the case has no practical importance, it may be remarked that essentially the same result is arrived at in the case of the single crystal rotation diagram. Here, ϕ itself has no cylindrical symmetry; $H(\mathbf{h})$ at any moment is dependent on the orientation of the crystal. We must now define the azimuth α of a vector $\mathbf{y}$ in the crystal with respect to a given crystal plane parallel to the rotation axis; the orientation of the crystal can be defined by the angle β between this crystal plane and the plane ($\mathbf{h}$; $\mathbf{z}$). What

we measure is the average over β of H, which brings the problem back to one of cylindrical symmetry:

$$\frac{H(\zeta,\xi)}{V}=\frac{1}{2\pi}\int_{\beta}\int_{\alpha}\int_{z}\int_{x}\phi(z,x,\alpha)$$
$$\times\exp\left[2\pi i\{\zeta z+\xi x\cos(\alpha+\beta)\}\right]x\,dx\,dz\,d\alpha\,d\beta.$$

Expanding,

$$\exp\{2\pi i\xi x\cos(\alpha+\beta)\}=\sum_{-\infty}^{+\infty}i^{l}I_{l}(2\pi\xi x)\exp\{il(\alpha+\beta)\},$$

and $$\phi(z,x,\alpha)=\sum_{-\infty}^{+\infty}\phi_{m}(z,x)\exp(-im\alpha). \quad (5)$$

The integration over α gives

$$\frac{H(\zeta,\xi)}{V}=\int_{\beta}\int_{z}\int_{x}\sum_{-\infty}^{+\infty}\phi_{l}(z,x)\,i^{l}I_{l}(2\pi\xi x)$$
$$\times\exp(il_{\beta}+2\pi i\zeta z)\,x\,dx\,dz\,d\beta.$$

Integrating over β, all terms of the sum over l give zero, with the exception of $l=0$:

$$\frac{H(\zeta,\xi)}{V}=2\pi\int_{z}\int_{x}\phi_{0}(z,x)\,I_{0}(2\pi\xi x)\exp(2\pi i\zeta z)\,x\,dx\,dz,$$

where, from (5),

$$\phi_{0}(z,x)=\frac{1}{2\pi}\int_{0}^{2\pi}\phi(z,x,\alpha)\,d\alpha.$$

This leads us back to the case of the fibre diagram, equation (1*b*).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Rapid publication will be easier if the contributions are without illustrations.

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A preliminary examination of the crystal structure of 2, 2′-bipyridyl and its relation to biphenyl.

By F. Wm. Cagle, Jr. *Institute for Advanced Study, Princeton, New Jersey, U.S.A.*

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Crystals of 2,2′-bipyridyl suitable for a single-crystal study are difficult to obtain. The material usually crystallizes in very complex aggregates. Small but satisfactory prisms were prepared by Prof. Francis H. Case, Temple University, Philadelphia, Pennsylvania. The compound had been carefully purified (m.p. 69–70° C.).

Rotation and Weissenberg patterns were taken about the *b*- and *c*-axes. The unit cell has the dimensions $a=5\cdot51$ A., $b=6\cdot24$ A., $c=13\cdot68$ A., $\beta=120°$. When indexed, the following interferences were found: *hkl* in all orders, *h*0*l* when $l=2n$, 0*k*0 when $k=2n$. These data are consistent with the choice of the space group $P2_1/c\text{–}C_{2h}^5$. The density of the crystals, determined by flotation in a solution of potassium iodide, was $1\cdot26$ g.cm.$^{-3}$ From this and the unit-cell dimensions we calculate that it contains 1·97 molecules. This indicates two molecules per unit cell and would require that these have a center of symmetry. This, taken with the observation (Feldman & Cagle, unpublished) that the ultra-violet spectrum of 2,2′-bipyridyl dissolved in a non-polar solvent is like that reported for biphenyl (O'Shaughnessy & Rodebush, 1940), indicates considerable resonance energy.

The entire problem of coplanarity of the benzene rings in biphenyl and its analogues, which are not substituted in the *o,o′*-positions, has attracted a great deal of interest. Pickett, Walter & France (1936), as well as O'Shaughnessy & Rodebush (1940) and Rodebush & Feldman (1946), have suggested, based on ultra-violet absorption data, that the rings of such compounds tend toward coplanarity.

On the other hand, Karle & Brockway (1944) have put forth objections to the coplanar structure for biphenyl. It was found that electron diffraction data could be fitted as well by a non-coplanar molecule as by a coplanar one. In addition, it was observed that one might expect some interference between the hydrogen atoms in the *o,o′*-positions.

In view of these facts, one is led to conclude that in solutions of compounds of this type, there is a definite tendency toward coplanarity. In the crystalline state this tendency results in coplanar molecules. It is significant to observe that there have been three published determinations of the space group of biphenyl (Clark & Pickett, 1931; Dhar, 1932; Hengstenberg & Mark, 1929). All of these agree that it is $P2_1/c\text{–}C_{2h}^5$ with two molecules per unit cell, and any error seems most unlikely.

In the case of 2,2′-bipyridyl, one concludes that the molecule exists in the crystal with the rings coplanar and with the nitrogen atoms *trans* to the bond joining the rings: